

# An Experimental and Theoretical Study of the Spin-orbit Interaction for $\text{CO}^+(\text{A}^2\Pi_{3/2,1/2}, v^+=0-41)$ and $\text{O}_2^+(\text{X}^2\Pi_{3/2,1/2g}, v^+=0-38)$

Y. Song, D. G. Fedorov, M. Evans, M. S. Gordon, and C. Y. Ng

Ames Laboratory, USDOE and Department of Chemistry,  
Iowa State University, Ames, IA 50011, USA

## INTRODUCTION

Accurate spin-orbit splitting constants ( $A_{v^+}$ ) for the vibrational levels  $v^+=0-41$  of  $\text{CO}^+(\text{A}^2\Pi_{3/2,1/2})$  have been determined in a rotationally resolved pulsed field ionization photoelectron study. A change in slope is observed in the  $v^+$  dependence for  $A_{v^+}$  at  $v^+\approx 19-20$ . This observation is attributed to perturbation of the  $\text{CO}^+(\text{A}^2\Pi)$  potential by the  $\text{CO}^+(\text{B}^2\Sigma^+)$  state. Theoretical  $A_{v^+}$  values for  $\text{CO}^+(\text{A}^2\Pi_{3/2,1/2}, v^+=0-41)$  have also been obtained using a newly developed *ab initio* computational routine for spin-orbit coupling calculations. The theoretical  $A_{v^+}$  predictions computed using this routine are found to be in agreement with the experimental  $A_{v^+}$  values for  $\text{CO}^+(\text{A}^2\Pi_{3/2,1/2}, v^+=0-41)$ . Similar  $A_{v^+}$  calculations obtained for  $\text{O}_2^+(\text{X}^2\Pi_{3/2,1/2g}, v^+=0-38)$  are also in accord with the recent experimental  $A_{v^+}$  values reported by Song *et al.*

## EXPERIMENTAL AND THEORETICAL METHODS

The design and performance of the Chemical Dynamics Beamline at the ALS and the multi-purpose photoelectron-photoion apparatus has been described previously.

*Ab initio* spin-orbit coupling calculations have been made possible by generalization of the existing spin-orbit coupling code built into the quantum chemistry package GAMESS. In order to accurately reproduce experimental results, a large basis set (AVTZ, built into MOLPRO) and an extensive CI wavefunction have been used. The orbitals are optimized with the complete active space self-consistent field (CASSCF) method, the active space including 12 electrons in 8 orbitals (2s and 2p on C and O). Energy values are further refined with single and double excitations from the CASSCF active space into the virtual space using MOLPRO. We have examined the effect of adding single and double excitations from the core 1s orbitals into virtual space: the  $\text{CO}^+$  results do not include such excitations and the  $\text{O}_2^+$  results do. Spin-orbit coupling calculations are performed with the CASSCF wavefunction and Pauli-Breit Hamiltonian, including rigorous one and two-electron terms and using the modified version of GAMESS soon to be released for distribution. The effect of including neighboring states into spin-orbit coupling diagonalization has been studied.  $\text{CO}^+$  calculations include the 6 lowest CI roots and  $\text{O}_2^+$  calculations include two roots.

The potential energy of  $\text{CO}^+(\text{A}^2\Pi)$  has been calculated for a series of internuclear C-O distances (R) of interest and a geometry optimization has been performed (at the CASSCF level) to locate the potential minimum. Experimentally, the splitting between the  $\text{CO}^+(\text{A}^2\Pi_{3/2})$  and  $\text{CO}^+(\text{A}^2\Pi_{1/2})$  spin-orbit states is found as a function of vibrational quantum number up to  $v^+=41$ . The rotational constants ( $B_{v^+}$ ) for  $\text{CO}^+(\text{A}^2\Pi_{3/2,1/2}, v^+=0-41)$  have also been determined.

A more sophisticated approach involves the least square fit of the calculated *ab initio* potential energies at a series of R values to a Morse potential. We find that these Morse potentials obtained based on the experimental vibrational energies for  $\text{CO}^+(\text{A}^2\Pi_{3/2,1/2})$  are in reasonable agreement with the  $\text{CO}^+(\text{A}^2\Pi)$  Morse potential based on the *ab initio* calculation. We note that the  $R_e$  value and the width of the theoretical  $\text{CO}^+(\text{A}^2\Pi)$  Morse potential are greater than the experimental  $\text{CO}^+(\text{A}^2\Pi_{3/2,1/2})$  Morse potentials. As a result, the outer turning point of the theoretical Morse potential is greater than that of the experimental Morse potential at the same

energy. We also list the Morse potential parameters for  $\text{CO}^+(\text{A}^2\Pi)$  constructed based on the vibrational constants cited in Huber and Herzberg. These parameters are in accord with those deduced from the present experiment.

The average vibrational energies for the  $\text{O}_2^+(\text{X}^2\Pi_{3/2,1/2g})$  spin-orbit states have been determined recently in a similar PFI-PE experiment by Song *et al.* The Morse potentials based on fitting to these experimental vibrational energies are given in Table I for comparison with the best fitted *ab initio* Morse potential for  $\text{O}_2^+(\text{X}^2\Pi)$ . As a reference, we also include in Table I the Morse potential for  $\text{O}_2^+(\text{X}^2\Pi)$  based on the vibrational constants cited in Huber and Herzberg. Similar to the observation for the  $\text{CO}^+(\text{A}^2\Pi)$  system, the theoretical  $R_e$  value is larger than that determined in the experiment. As a result, the outer wall of the theoretical Morse potential for  $\text{O}_2^+(\text{X}^2\Pi)$  is wider than that for the experimental Morse potential.

The  $A(R)$  function for the  $\text{O}_2^+(\text{X}^2\Pi)$  system has the form:  $A(R) = h \exp[-s(R - R_0)^2] + A_0$ . The least square fit parameters are,  $h = 138.219$ ,  $A_0 = 1.06641$ ,  $R_0 = 1.0115$ , and  $s = 58.9876$ .

## RESULTS

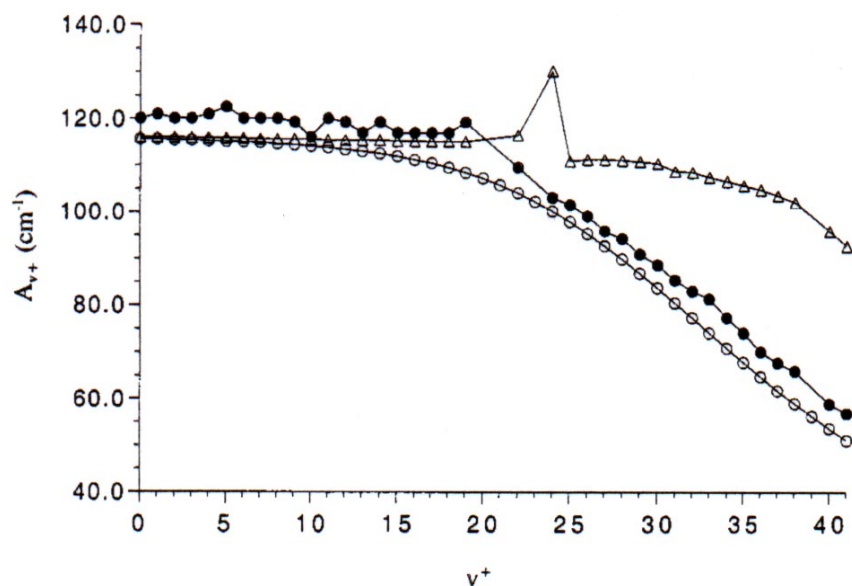


Figure 1. Plot of the experimental and theoretical spin-orbit splitting constants ( $A_{v+}$ ) for  $\text{CO}^+(\text{A}^2\Pi_{3/2,1/2})$  versus  $v^+$  in the range of  $v^+=0-41$ . Experimental values are in solid circles. The theoretical values obtained using the *ab initio* Morse potential and by the single-point approach are shown as open circles and triangles, respectively.

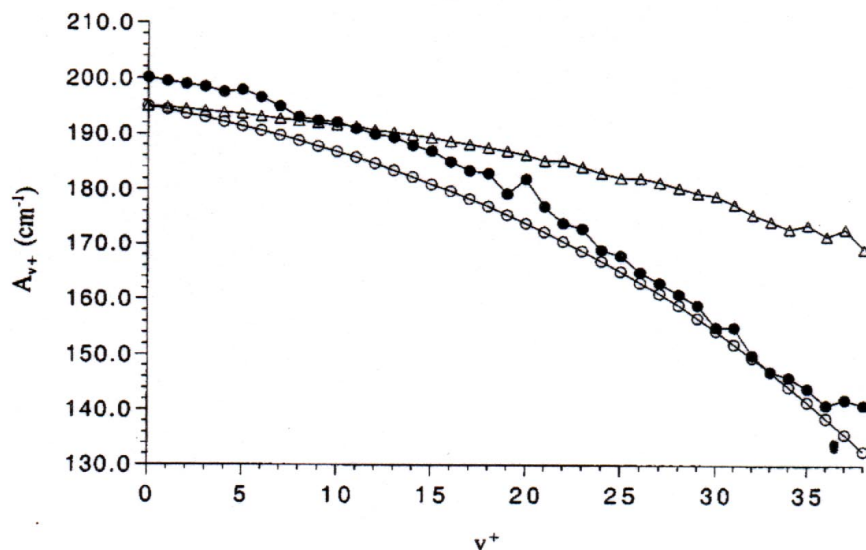


Figure 2. Plot of the experimental and theoretical spin-orbit splitting constants ( $A_{v+}$ ) for  $\text{O}_2^+(\text{A}^2\Pi_{3/2,1/2})$  versus  $v^+$  in the range of  $v^+=0-38$ . Experimental values are in solid circles. The theoretical values obtained using the *ab initio* Morse potential and by the single-point approach are shown as open circles and triangles, respectively.

### A. $\text{CO}^+(\text{A}^2\Pi_{3/2,1/2}, v^+=0-41)$

We have obtained rotationally resolved PFI-PE bands for  $\text{CO}^+(\text{A}^2\Pi_{3/2,1/2}, v^+=0-41)$ . The  $A_{v^+}$  values for  $\text{CO}^+(\text{A}^2\Pi_{1/2}, v^+=0-41)$  are obtained by the BOS simulation. The plot of the experimental  $A_{v^+}$  value versus  $v^+$  is shown in Fig. 1. It is interesting to note that the  $A_{v^+}$  value seems to remain nearly constant until  $v^+\approx 19$ , which has an IE value of 19.6 eV. Then it decreases nearly linearly toward higher  $v^+$ . As shown in Fig. 3, for  $v^+\leq 19$  the single-point theoretical predictions and the experimental results are in slightly better accord than those obtained based on the theoretical Morse potential. However, the predictions for  $v^+>19$  obtained by the single-point approach deviate significantly lower from the experimental values. This discrepancy observed at high  $v^+$  is expected and can be attributed to the increasing anharmonicity of the  $\text{CO}^+(\text{A}^2\Pi)$  potential at high  $v^+$ . The theoretical predictions obtained using the theoretical Morse potential show the correct overall  $v^+$  dependence for  $A_{v^+}$ . The theoretical  $A_{v^+}$  value varies smoothly over the whole  $v^+$  range. Contrary to the experimental observation, the  $v^+$  dependence for the theoretical  $A_{v^+}$  values shows no break at  $v^+\approx 19-20$ .

### B. $\text{O}_2^+(\text{X}^2\Pi_{3/2,1/2g}, v^+=0-38)$

The theoretical  $A_{v^+}$  predictions obtained here based on the single-point approach and the *ab initio* Morse potential are plotted in Fig. 2 for comparison with the experimental  $A_{v^+}$  values for  $\text{O}_2^+(\text{X}^2\Pi_{3/2,1/2g}, v^+=0-38)$ . The latter values have been reported recently by Song *et al.* The trend of the  $v^+$  dependence for the theoretical  $A_{v^+}$  value obtained using the *ab initio* Morse potential is consistent with the experimental data. Although the theoretical predictions based on the *ab initio* Morse potential and experimental  $A_{v^+}$  values are in general agreement, all theoretical predictions are slightly lower than the corresponding experimental results.

The  $A_{v^+}$  values for  $\text{O}_2^+(\text{X}^2\Pi_{3/2,1/2g}, v^+=20)$  determined in both the synchrotron based PFI-PE and VUV laser PFI-PE studies are higher than the  $A_{v^+}$  values for the adjacent  $v^+=19$  and 20 states. Thus, the variation of  $A_{v^+}$  versus  $v^+$  is most likely not a smooth function. We note this kink observed at  $\text{O}_2^+(\text{X}^2\Pi_{3/2,1/2g}, v^+=20)$  with an IE  $\approx 15.96$  eV is also close to the beginning of the vibrational progression of the  $\text{O}_2^+(\text{a}^4\Pi_u)$  state beginning at  $\approx 16.10$  eV. The latter PFI-PE band is nearly in total overlap with the  $\text{O}_2^+(\text{X}^2\Pi_{3/2,1/2g}, v^+=21)$  state. The  $A_{v^+}$  values for  $\text{O}_2^+(\text{X}^2\Pi_{3/2,1/2g}, v^+=37$  and 38), which have the IEs  $\approx 17.9-18.0$  eV, also seem to deviate from the general trend of the  $A_{v^+}$  versus  $v^+$  curve. This observation may be correlated to the appearance of the vibrational progression for the  $\text{O}_2^+(\text{b}^4\Sigma_g^-)$  state at 18.1 eV. On the basis of this observation, we tentatively attribute this kink at  $\text{O}_2^+(\text{X}^2\Pi_{3/2,1/2g}, v^+=20)$  and  $\text{O}_2^+(\text{X}^2\Pi_{3/2,1/2g}, v^+=37-38)$  as due to perturbation by the  $\text{O}_2^+(\text{a}^4\Pi_u)$  and  $\text{O}_2^+(\text{b}^4\Sigma_g^-)$  states, respectively. This speculation requires theoretical confirmations in the future.

## REFERENCE

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2. M. Evans and C. Y. Ng, *J. Chem. Phys.*, submitted.

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Principal investigator: Prof. C.Y. Ng, Ames Laboratory, USDOE and Department of Chemistry, Iowa State University, Ames, IA 50011, USA. Email: [cyng@ameslab.gov](mailto:cyng@ameslab.gov). Telephone: 515-294-4225